

1. A process to form damascene structures, comprising:

providing a substrate having an upper surface in which are a plurality of trenches that have at least two different widths, said trenches having a conductive surface;

- 5 providing a first electrolytic solution, whose composition has been optimized for filling trenches whose width is less than about 0.2 microns, and a second electrolytic solution, whose composition has been optimized for filling trenches whose width is greater than about 1 micron;

- 10 electroplating from said first solution a sufficient thickness of a metal to overfill all trenches whose width is less than about 0.2 microns while under-filling all trenches whose width is greater than about 1 microns; and

then electroplating from said second solution a sufficient thickness of said metal to overfill all trenches.

2. The process described in claim 1 wherein said first electrolytic solution further comprises a short chain polymer having low molecular weight.

- 15 3. The process described in claim 1 wherein said second electrolytic solution further comprises a long chain polymer having high molecular weight.

4. A process for filling trenches with copper, comprising:

providing a silicon wafer having an upper surface in which are a plurality of

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trenches that have at least two different widths, all trenches being lined with a conductive barrier layer;

providing an aqueous solution that comprises at least one copper salt;

forming a first plating solution that contains a first concentration, in said aqueous solution, of a first accelerator additive;

forming a second plating solution that contains a second concentration, in said aqueous solution, of a second accelerator additive, said second concentration being greater than said first concentration;

in a first bath that contains said first plating solution, electroplating onto said upper surface a first thickness of copper that is sufficient to overfill all trenches whose width is less than an amount while under-filling all trenches whose width is greater than said amount; and

then transferring said wafer to a second bath that contains said second plating solution and electroplating on the wafer a second thickness of copper that is sufficient to overfill all trenches.

5 The process described in claim 4 wherein said aqueous solution further comprises 10-50 g/L copper salts, 5-300 g/LH₂SO₄, and 20-100 ppm HCl.

6. The process described in claim 4 wherein said amount is between about 0.2 and 1 microns.

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7. The process described in claim 4 wherein said first accelerator additive is at a concentration that is between about 10-100 ppm.

8. The process described in claim 4 wherein said second accelerator additive is 3-sulfopropyl disulfide.

5 9. The process described in claim 8 wherein said second accelerator additive concentration is between about 10-100 ppm.

10. The process described in claim 4 wherein said second accelerator additive is sulfonated acetylthiourea, 3-mercapto-1-propanesulfonate, dibenzyl-dithio-carbammat, 2-mercaptoethanesulfonate, or n,n - dimethyl-dithiocabamic acid-(3-sulfopropyl)ester.

10 11. The process described in claim 4 wherein said first thickness of electroplated copper is between about 0.1 and 0.2 microns.

12. The process described in claim 4 wherein said second thickness of electroplated copper is between about 0.2 and 0.5 microns.

13. The process described in claim 4 wherein said conductive barrier layer is TiN, Ta/Ti/TaN, or WN.
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14. A process for filling trenches with copper, comprising:

providing a silicon wafer having an upper surface in which are a plurality of trenches that have at least two different widths, all trenches being lined with a seed layer;

providing an aqueous solution that comprises at least one copper salt;

5 forming a first plating solution that contains a first concentration, in said aqueous solution, of a first accelerator additive;

forming a second plating solution that contains a second concentration, in said aqueous solution, of a second accelerator additive, said second concentration being greater than said first concentration;

10 in a first bath that contains said first plating solution, electroplating onto said seed layer a first thickness of copper that is sufficient to overfill all trenches whose width is less than an amount while under-filling all trenches whose width is greater than said amount; and

then transferring said wafer to a second bath that contains said second plating solution and electroplating on the wafer a second thickness of copper that is sufficient to overfill all trenches.

15 The process described in claim 14 wherein said aqueous solution further comprises 10-50 g/L copper salts, 5-300 g/L H_2SO_4 , and 20-100 ppm HCl.

16. The process described in claim 14 wherein said amount is between about 0.2 and

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1 microns].

17. The process described in claim 14 wherein said first accelerator additive is (3-sulfopropyl) disulfide, 3-mercapto-propylsulfonic at a concentration that is between about 10 and 100 ppm.

5 18. The process described in claim 14 wherein said second accelerator additive is 3sulfopropyl disulfide.

19. The process described in claim 18 wherein said second accelerator additive concentration is between about 10-100 ppm.

10 20. The process described in claim 14 wherein said second accelerator additive is sulfonated acetylthiourea, 3-mercapto-1propanesulfonate, dibenzyl-dithio-carbammat, 2-mercaptoethanesulfonate, or n,n - dimethyl-dithiocabamic acid-(3-sulfopropyl)ester.

21. The process described in claim 14 wherein said first thickness of electroplated copper is between about 0.1 and 0.2 microns.

15 22. The process described in claim 14 wherein said second thickness of electroplated copper is between about 0.3 and 0.5 microns.

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23. The process described in claim 14 wherein said seed layer is copper.

24. The process described in claim 14 wherein said seed layer is copper doped with titanium, magnesium, zirconium, tin, or zinc..

25. A process for filling trenches with copper, comprising:

5 providing a silicon wafer having an upper surface in which are a plurality of trenches that have at least two different widths, all trenches being lined with a conductive barrier layer;

providing an aqueous solution that comprises at least one copper salt;

10 forming a first plating solution that contains a first concentration, in said aqueous solution, of a first accelerator additive;

forming a second plating solution that contains a second concentration, in said aqueous solution, of a second accelerator additive, said second concentration being greater than said first concentration;

15 filling a container with said first plating solution and immersing said wafer therein, then electroplating onto said upper surface a first thickness of copper that is sufficient to overfill all trenches whose width is less than an amount while under-filling all trenches whose width is greater than said amount;

while leaving said wafer in container, replacing said first plating solution with said second plating solution; and

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then electroplating on said wafer a second thickness of copper that is sufficient to overfill all trenches.

26. The process described in claim 25 wherein the step, of replacing said first plating solution with said second plating solution, further comprises a continuous change in
5 accelerator concentration without interruption of electroplating.

27. The process described in claim 25 wherein said aqueous solution further comprises 10-50 g/L copper salts, 5-300 g/L H_2SO_4 , and 20-100 ppm HCl.

28. The process described in claim 25 wherein said first accelerator additive is 3-mercapto-1propanesulfonate at a concentration that is between about 10 and 100 ppm.

10 29. The process described in claim 25 wherein said second accelerator additive is 3sulfopropyl disulfide.

30. The process described in claim 29 wherein said second accelerator additive concentration is between about 10-100 ppm.

31. The process described in claim 25 wherein said accelerator additive is sulfonated
15 sulfonated acetylthiourea, 3-mercapto-1propanesulfonate, dibenzyl-dithio-carbammat,

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2-mercaptoethanesulfonate, or n,n - dimethyl-dithiocabamic acid-(3-sulfopropyl)ester.

32. A process for filling trenches with copper, comprising:

providing a silicon wafer having an upper surface in which are a plurality of trenches that have at least two different widths, all trenches being lined with a seed layer;

5 providing an aqueous solution that comprises at least one copper salt;

forming a first plating solution that contains a first concentration, in said aqueous solution, of a first accelerator additive;

forming a second plating solution that contains a second concentration, in said aqueous solution, of a second accelerator additive, said second concentration being
10 greater than said first concentration;

filling a plating bath with said first plating solution and immersing said wafer therein, then electroplating onto said seed layer a first thickness of copper that is sufficient to overfill all trenches whose width is less than an amount while under-filling all trenches whose width is greater than said amount;

15 while leaving said wafer in said plating bath, replacing said first plating solution with said second plating solution; and

then electroplating on said wafer a second thickness of copper that is sufficient to overfill all trenches.

33. The process described in claim 32 wherein the step, of replacing said first plating

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solution with said second plating solution, further comprises a continuous change in accelerator concentration without interruption of electroplating.

34. The process described in claim 32 wherein said aqueous solution further comprises 10-50 g/L copper salts, 5-300 g/L H_2SO_4 , and 20-100 ppm HCl.

5 35. The process described in claim 32 wherein said first accelerator additive is (3-sulfopropyl) disulfide, 3-mercapto-propylsulfonic at a concentration that is between about 10-100 ppm.

36. The process described in claim 32 wherein said second accelerator additive is 3-sulfopropyl disulfide.

10 37. The process described in claim 36 wherein said second accelerator additive concentration is between about 10-100 ppm.

38. The process described in claim 4 wherein said second accelerator additive is sulfonated acetylthiourea, 3-mercapto-1-propanesulfonate, dibenzyl-dithio-carbammat, 2-mercaptoethanesulfonate, or n,n - dimethyl-dithiocabamic acid-(3-sulfopropyl)ester.

15 39. The process described in claim 32 wherein said seed layer is copper, or copper doped with titanium, magnesium, zirconium, tin, or zinc.